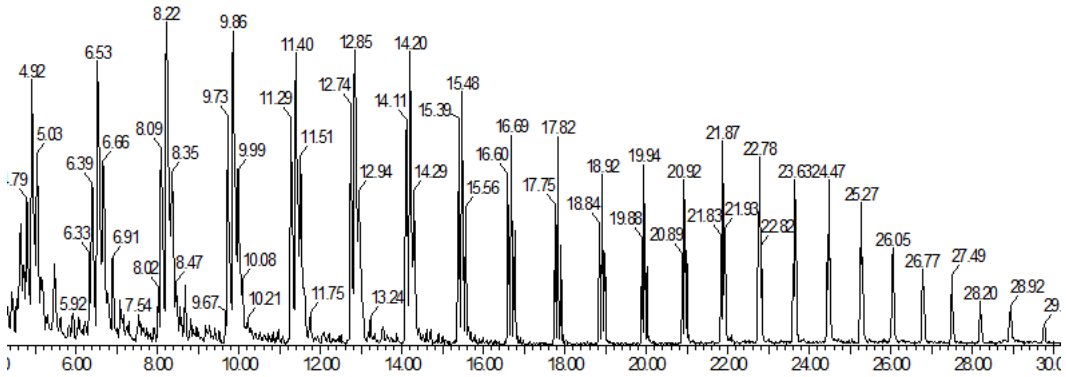
Microplastics identification by pyrolysis gas chromatography mass spectrometry (py-GCMS)

Presented by John W Scott, ISTC Senior Analytical Chemist



Polyethylene

Plastic -Designed to Last Forever, Yet Intended for Single Use

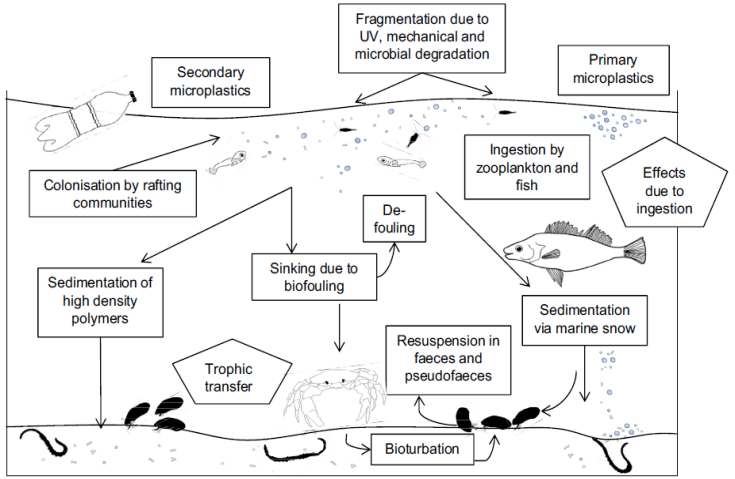
- Cumulative plastic waste generated is 6.3 billion metric tons[1].
- 79% of this material deposited in landfills and the natural environment[1].
- Microplastics are now ubiquitous in the environment.
- Models predict that 50% of the plastics found in European seas are more than 17 years of age[2].

1 - Geyer, Roland, Jenna R. Jambeck, and Kara Lavender Law. "Production, use, and fate of all plastics ever made." Science advances 3, no. 7 (2017): e1700782.

2- Koelmans, Albert A., Adil Bakir, G. Allen Burton, and Colin R. Janssen. "Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies." Environmental science & technology 50, no. 7 (2016): 3315-3326.

The Impact of Environmental Plastics

- Adverse effects on humans and wildlife currently under investigation. Some studies show neutral effects, others show negative effects[3].
- Vectors for chemical exposure to POPs, emerging contaminants, etc.
- Vectors for pathogens and viruses.
- Economic losses in tourism and fisheries[4,5].
- Identification of the materials present in the environment is important for source appointment, risk assessment, abatement and wildlife management



Wright, S. L., R. C. Thompson, and T. S. Galloway. 2013. The physical impacts of microplastics on marine organisms: A review. Environmental Pollution 178:483–492.

3- Foley, Carolyn J., Zachary S. Feiner, Timothy D. Malinich, and Tomas O. Höök. "A meta-analysis of the effects of exposure to microplastics on fish and aquatic invertebrates." *Science of the Total Environment* 631 (2018): 550-559.

4- Mouat, J., Lozano, R. L. & Bateson, H. (2010). *Economic Impacts of marine litter*. KIMO International, pp. 105.

Beaumont, Nicola J., Margrethe Aanesen, Melanie C. Austen, Tobias Börger, James R. Clark, Matthew Cole, Tara Hooper, Penelope K. Lindeque, Christine Pascoe, and Kayleigh J. Wyles. "Global ecological, social and economic impacts of marine plastic." *Marine Pollution Bulletin* 142 (2019): 189-195.

Identification of Microplastics

FT-IR Microscope

Versus

pyGCMS

- Short Analysis Time (Minutes)
- Can analyze samples directly on filter
- Analysis is Non-Destructive
- Can be problematic with small sample sizes
- Difficulty with some materials (i.e. rubbers)
- Limited information

- Long Analysis Time(~ 1 hour)
- Samples have to be removed from filters
- Destructive
- Can analyze small samples (100 μg or less)
- Can detect a wider range of materials
- More detailed information

Analytical Pyrolysis – The Theory Behind the Technique

Degradation Mechanisms

- Random Scission – Example Polyolefin

(S1) -C-C-C-C-C-C

(S2) -C-C-C▪ ▪C-C-C-

(S3) -C-C-C(▪)-C-C-C-

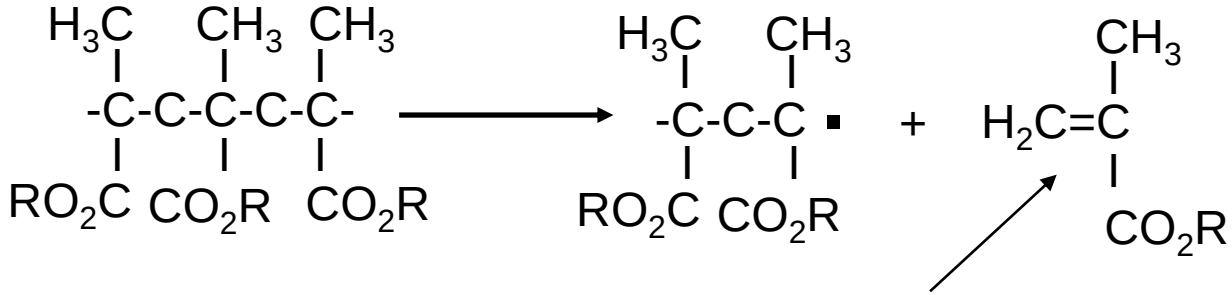
(S4) -C-C-C=CH_2 + ▪C-C-

Major products – Hydrocarbons (saturated, with one terminal double bond, and with two terminal double bonds)

- Side Group Scission – Example polyvinyl chloride

Major products – Aromatics (benzene, toluene, naphthalene) and chlorinated aromatics.

- Monomer Reversion– Example poly(methyl methacrylate)



Major products – Methyl methacrylate

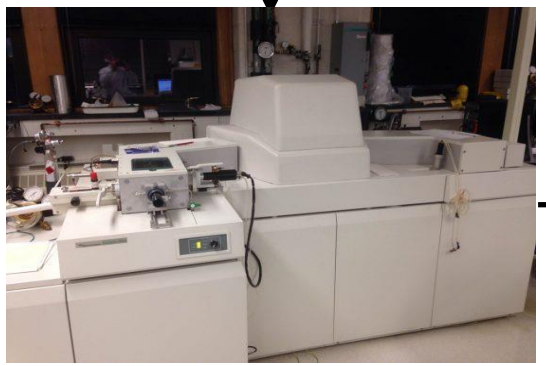
pyGCMS - Instrumentation

Load Material in Quartz Capillary Tube

Pyrolysis products

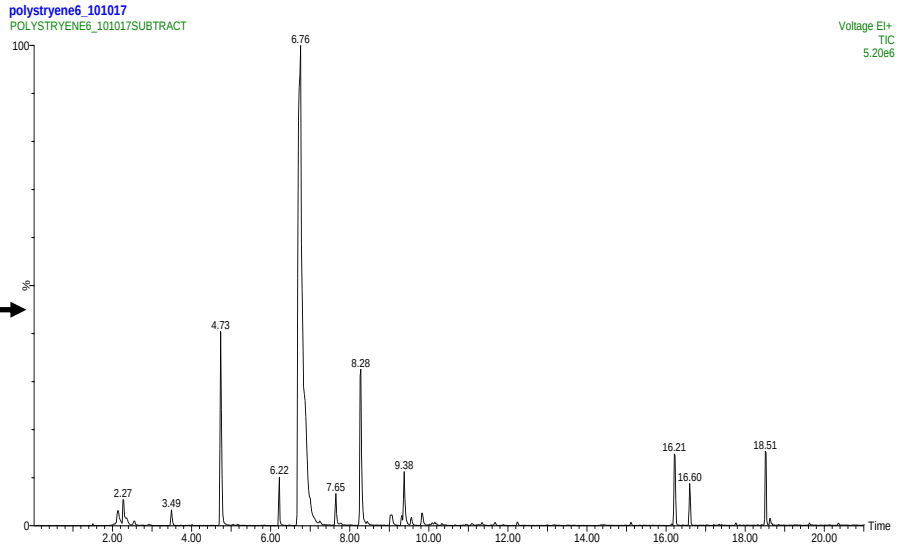
Transfer Line

Separate products with GC

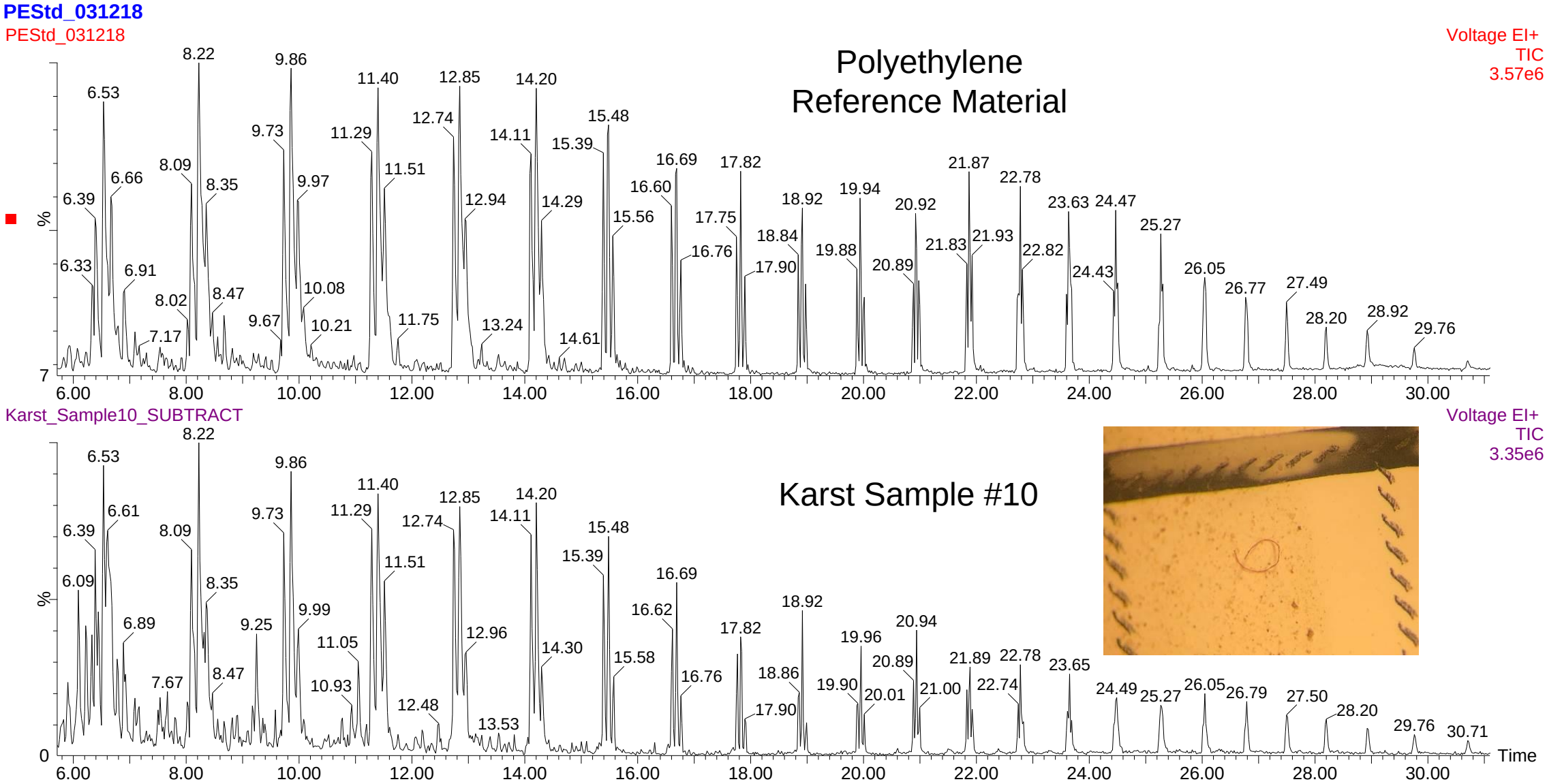


Detection by Mass Spectrometry

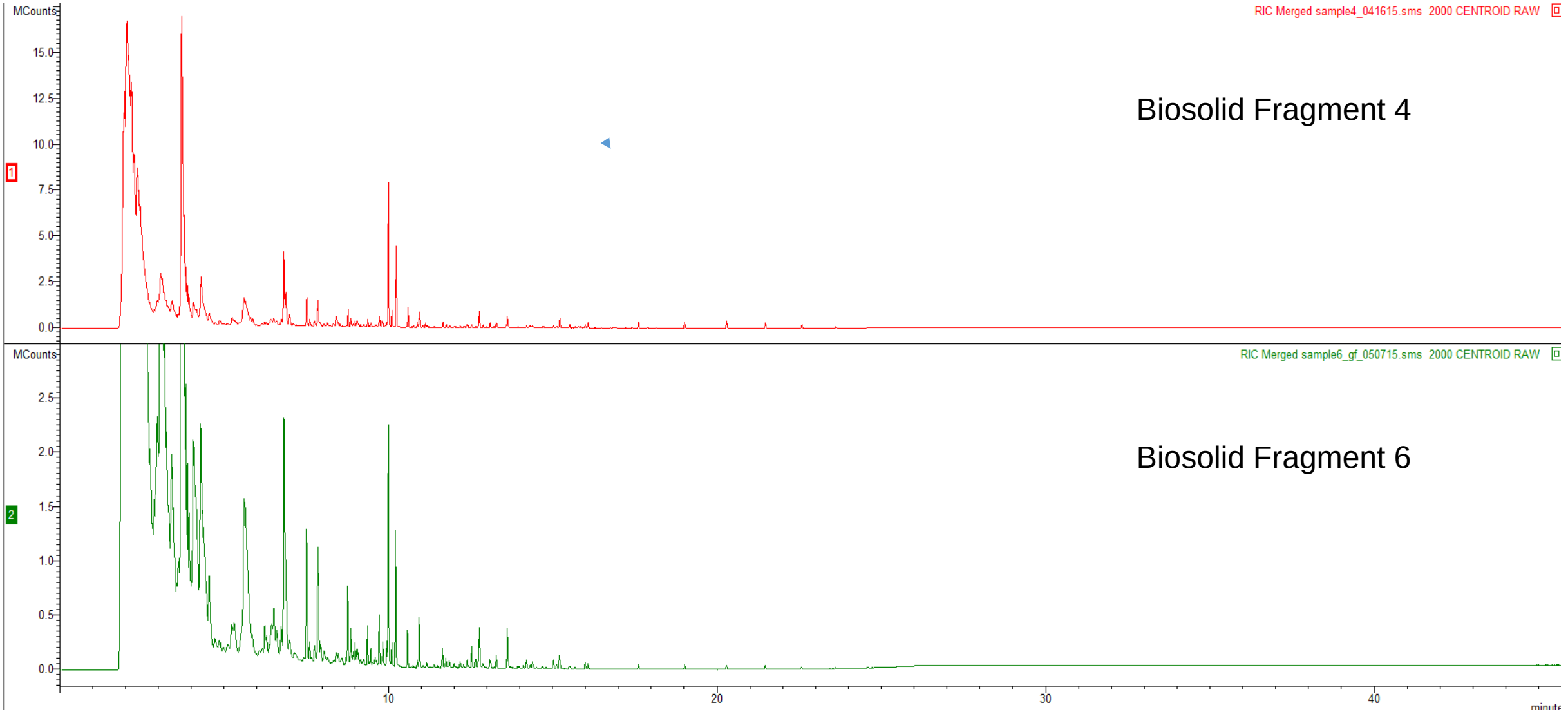
Pyrogram



Karst Water – Microplastic Pyrogram



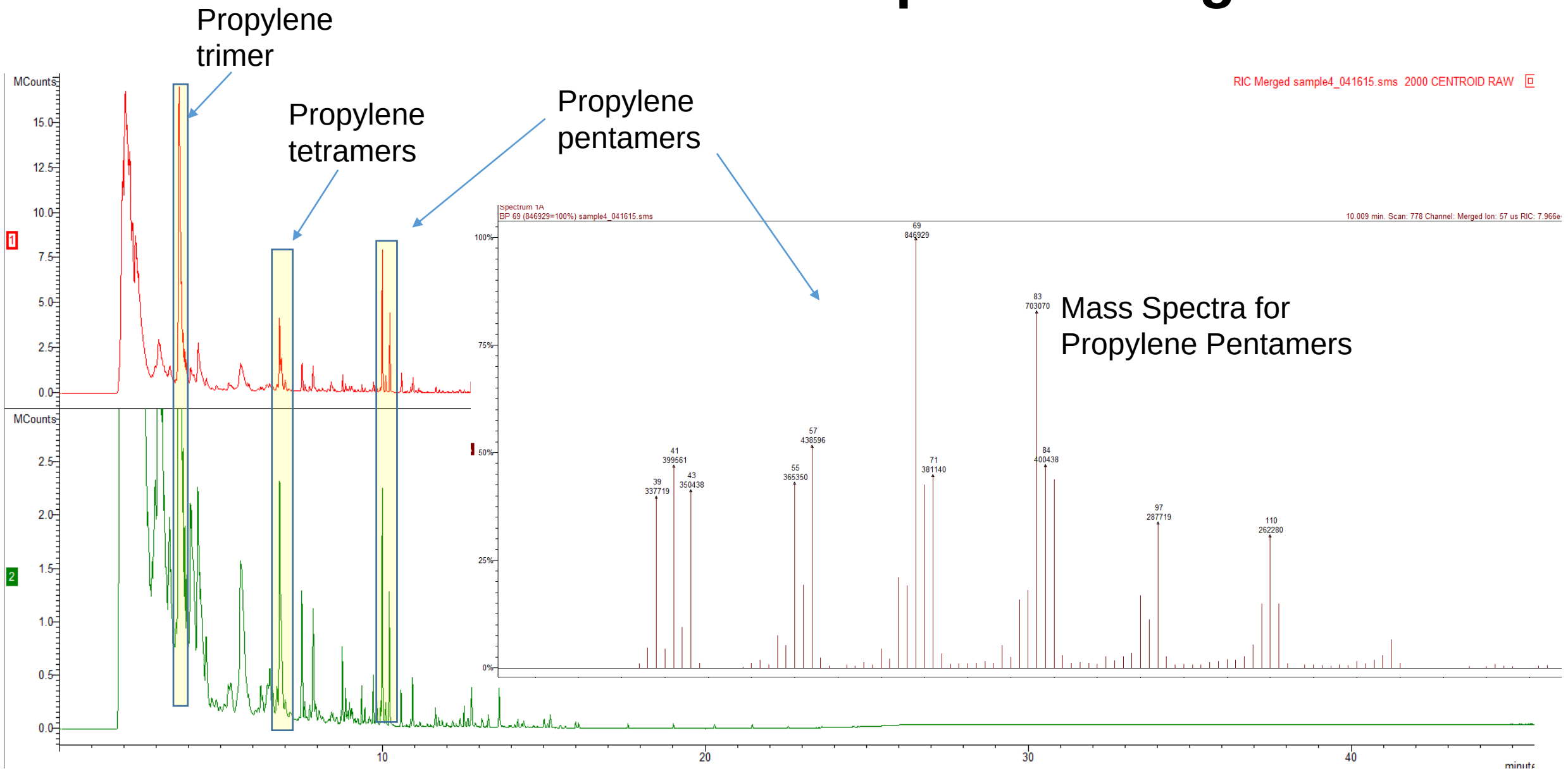
Biosolids– Microplastic Fragments



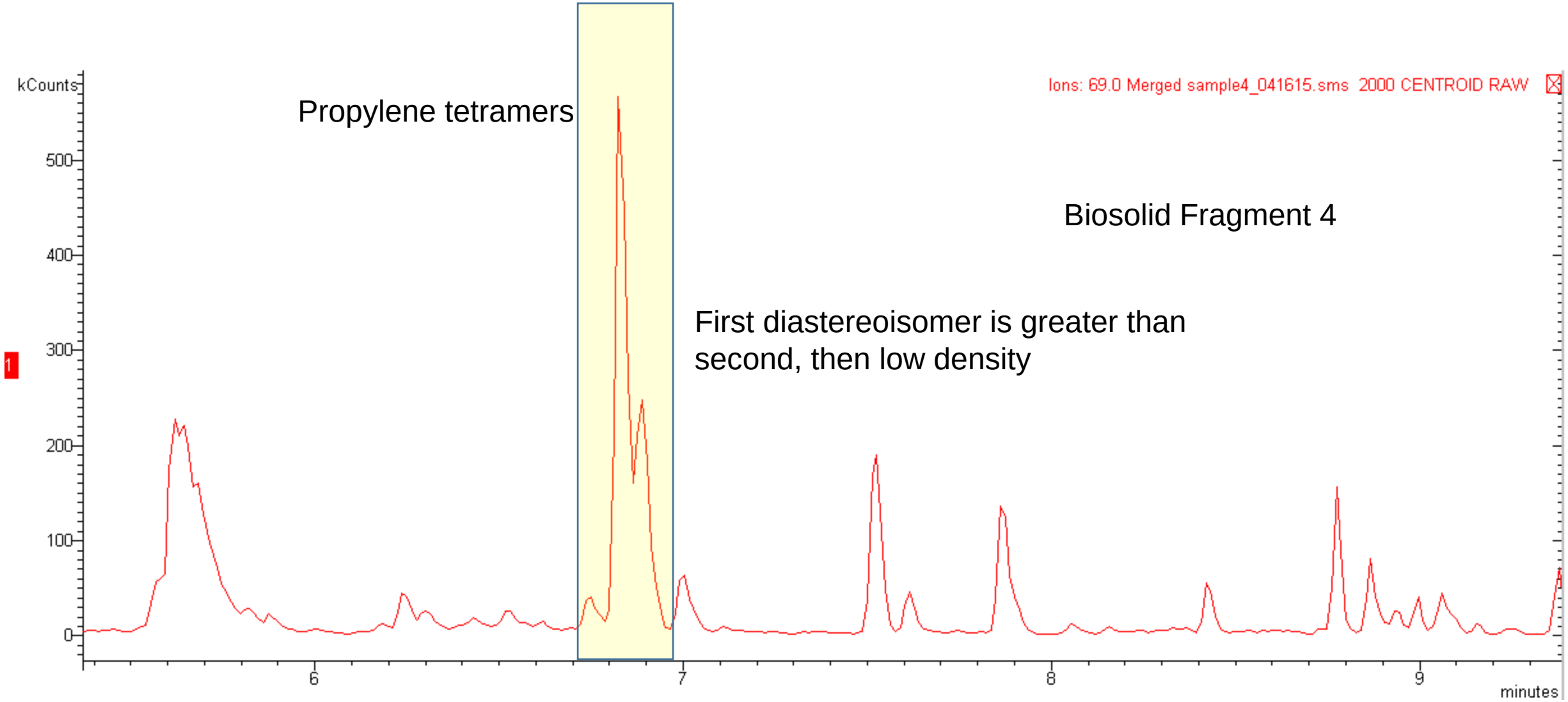
Biosolid Fragment 4

Biosolid Fragment 6

Biosolids– Microplastic Fragments

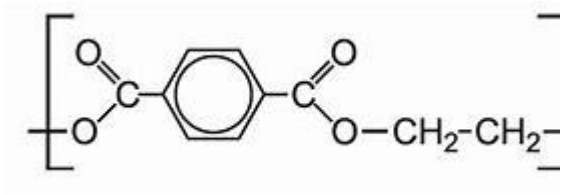


Propylene Tetramers – Low Density versus High Density



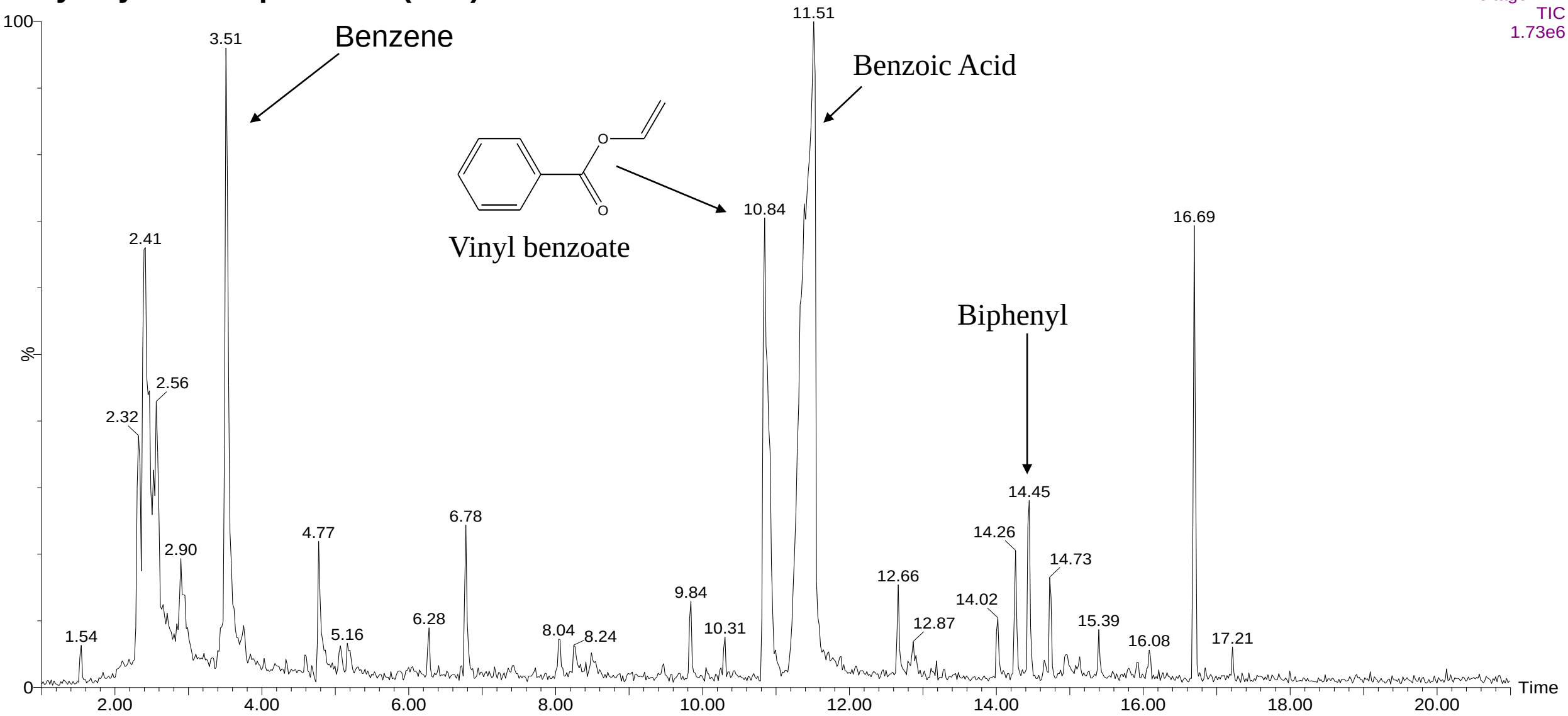
Moldoveanu, Serban. *Analytical pyrolysis of synthetic organic polymers*. Vol. 25. Elsevier, 2005.

Polyesters



Polyethylene terephthalate (PET)

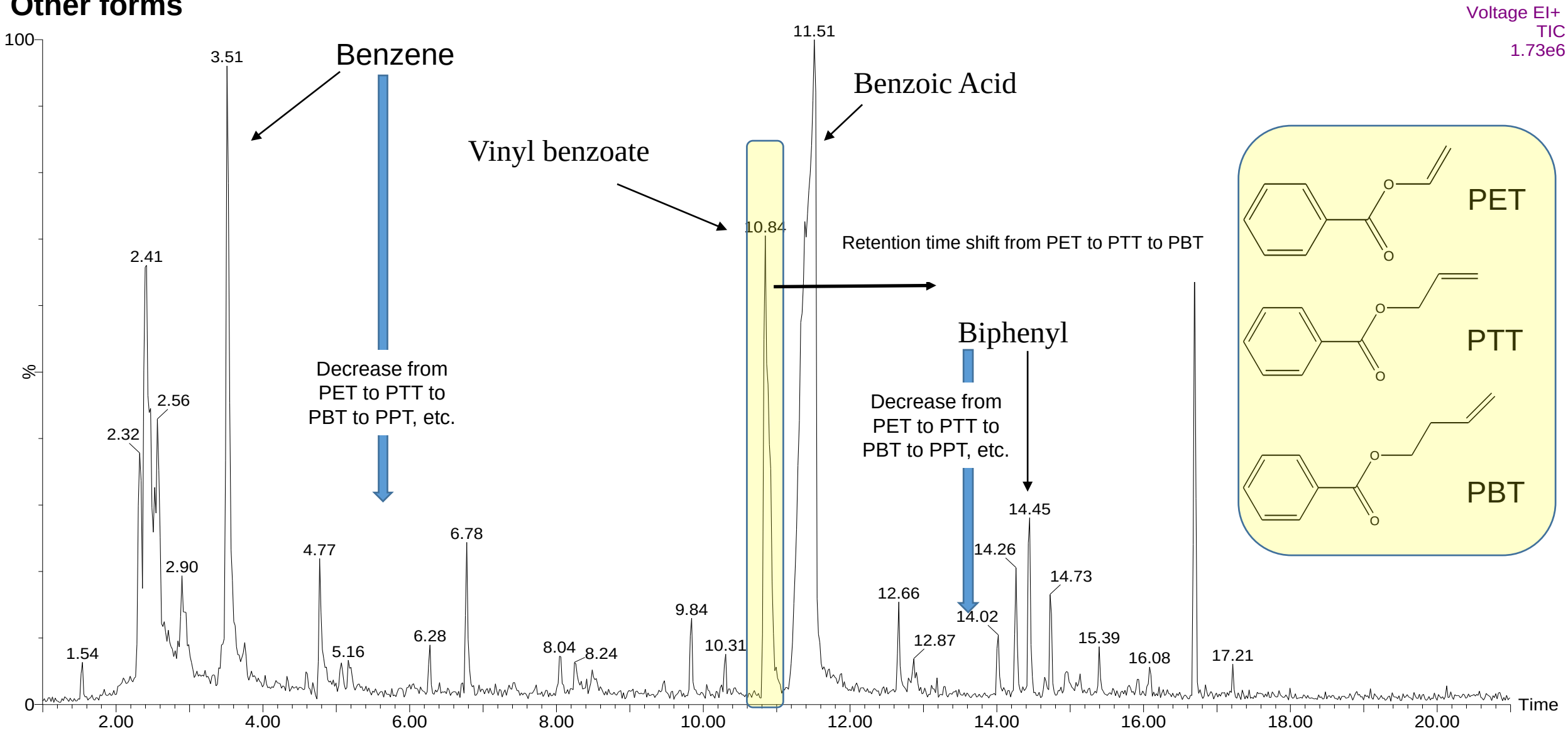
Voltage EI+
TIC
1.73e6



Wampler, Thomas P. *Applied pyrolysis handbook*. CRC press, 2006.

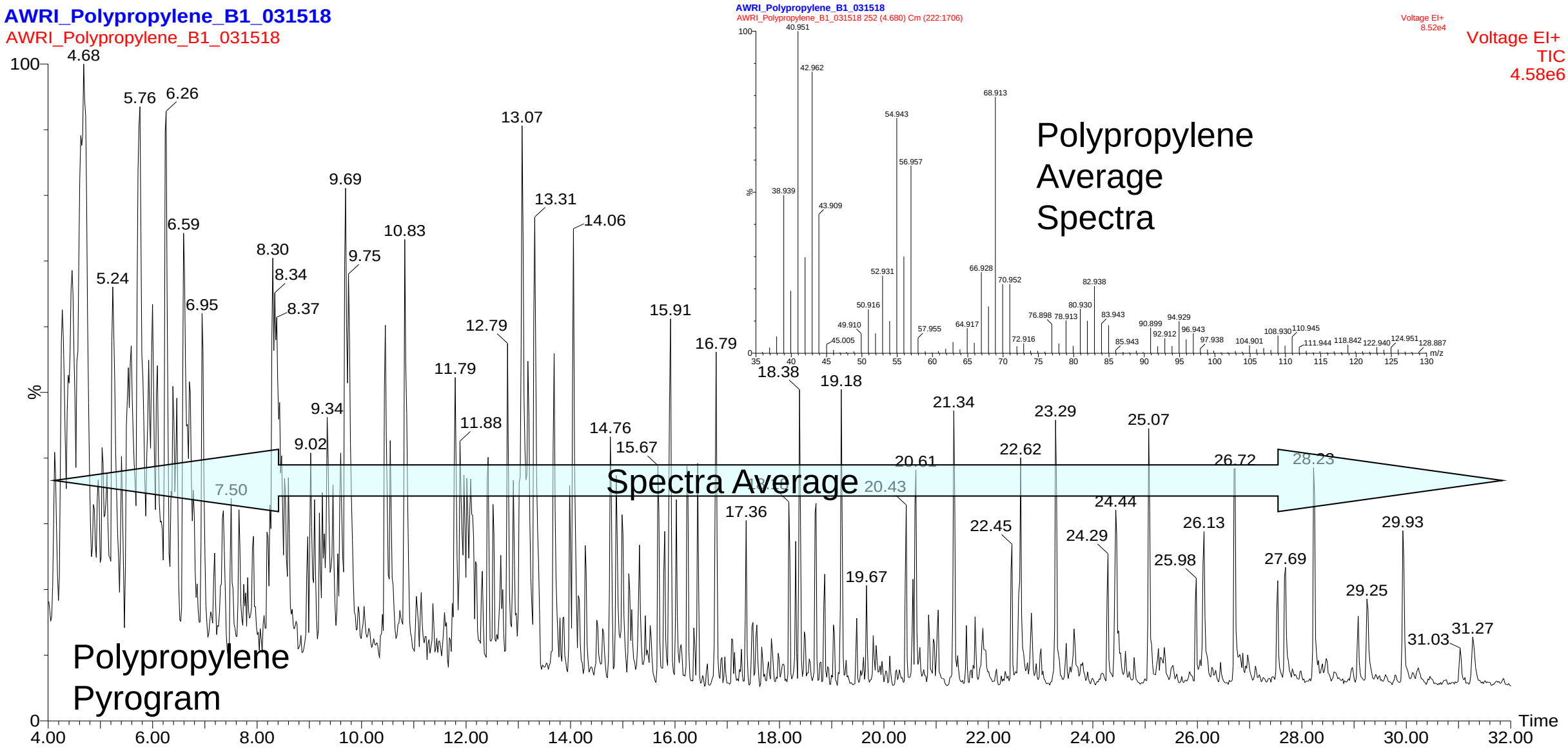
Polyesters

Other forms

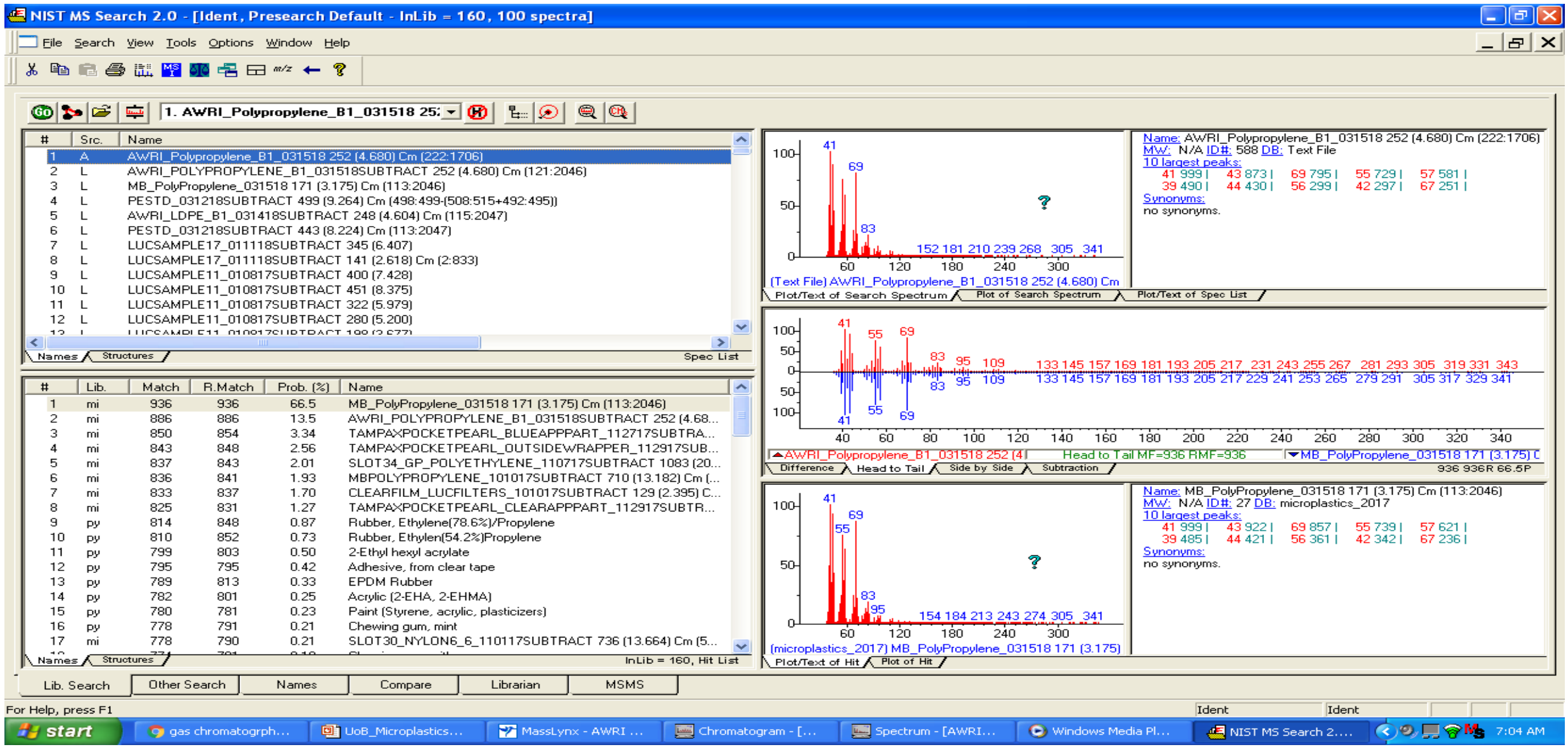


Wampler, Thomas P. *Applied pyrolysis handbook*. CRC press, 2006.

Spectra Averaging to Facilitate Library Searching



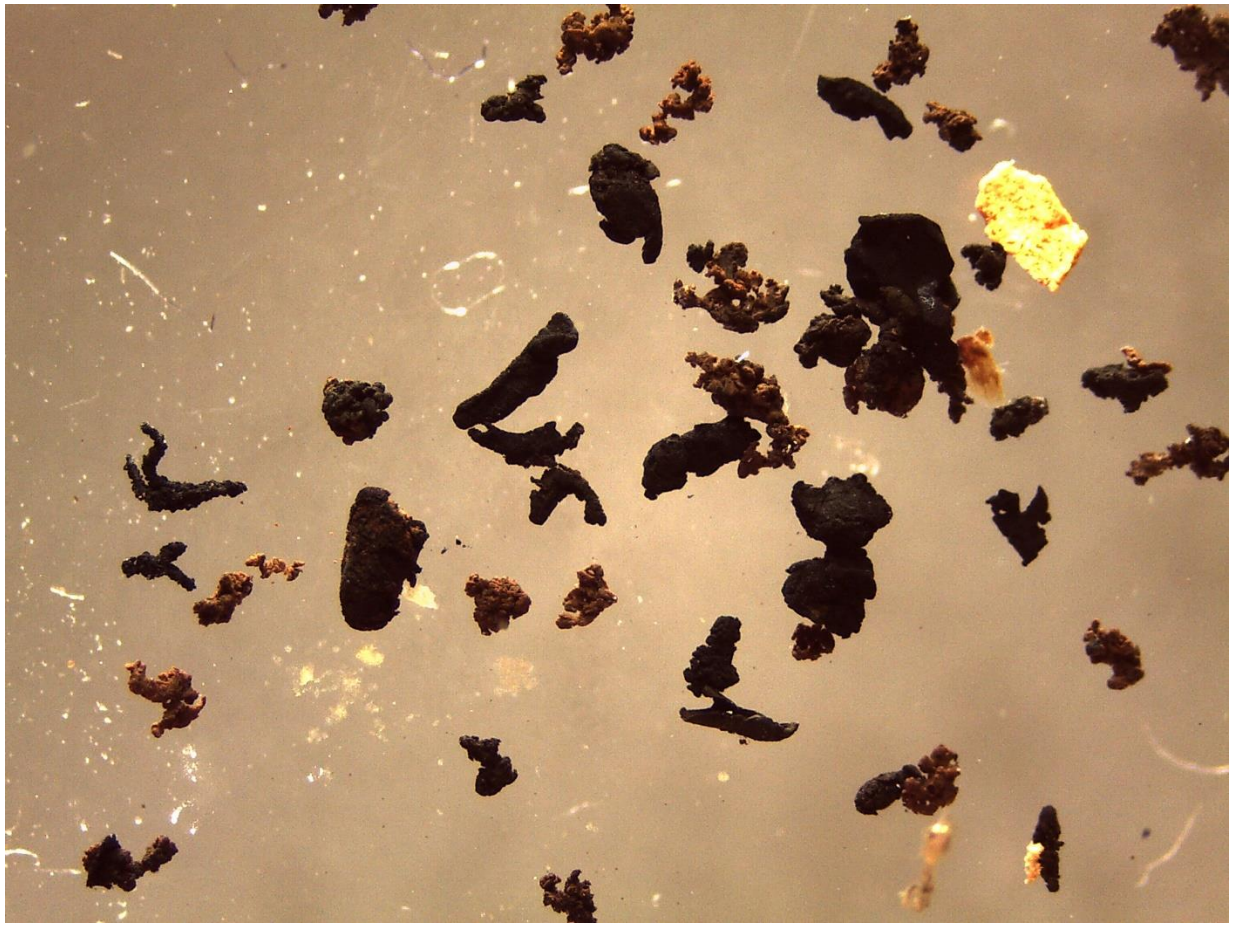
Database Searching of Pyrograms

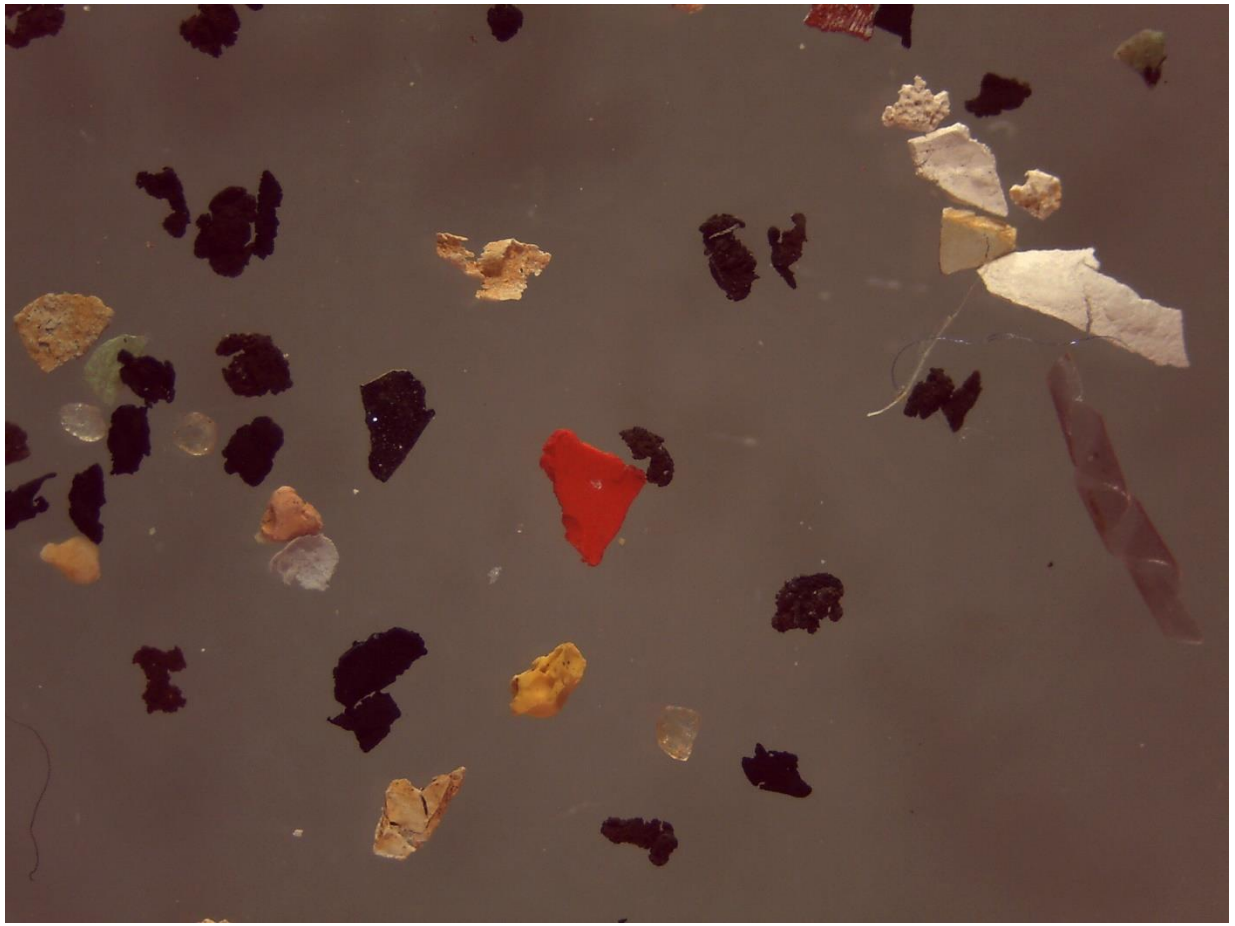


Examples: In-House Microplastics Database at ISTC

Ref #	Material
12	Kimberly Clark Purple Nitrile Glove
13	Tampax Pocket Pearl - Blue Applicator
14	Tampax Pocket Pearl - Inside White Absorbant
15	Tampax Pocket Pearl - Clear Part of Applicator
16	Tampax Pocket Pearl - Wrapper
17	Polylactic Acid from Clear Cup Plastic #7
18	Lube from Basic Condom
19	Whole Condom Right Out of Package
20	Basic Condom Outside Wrapper
21	Basic Condom Whole, lube extracted
22	Polycarbonate from CD

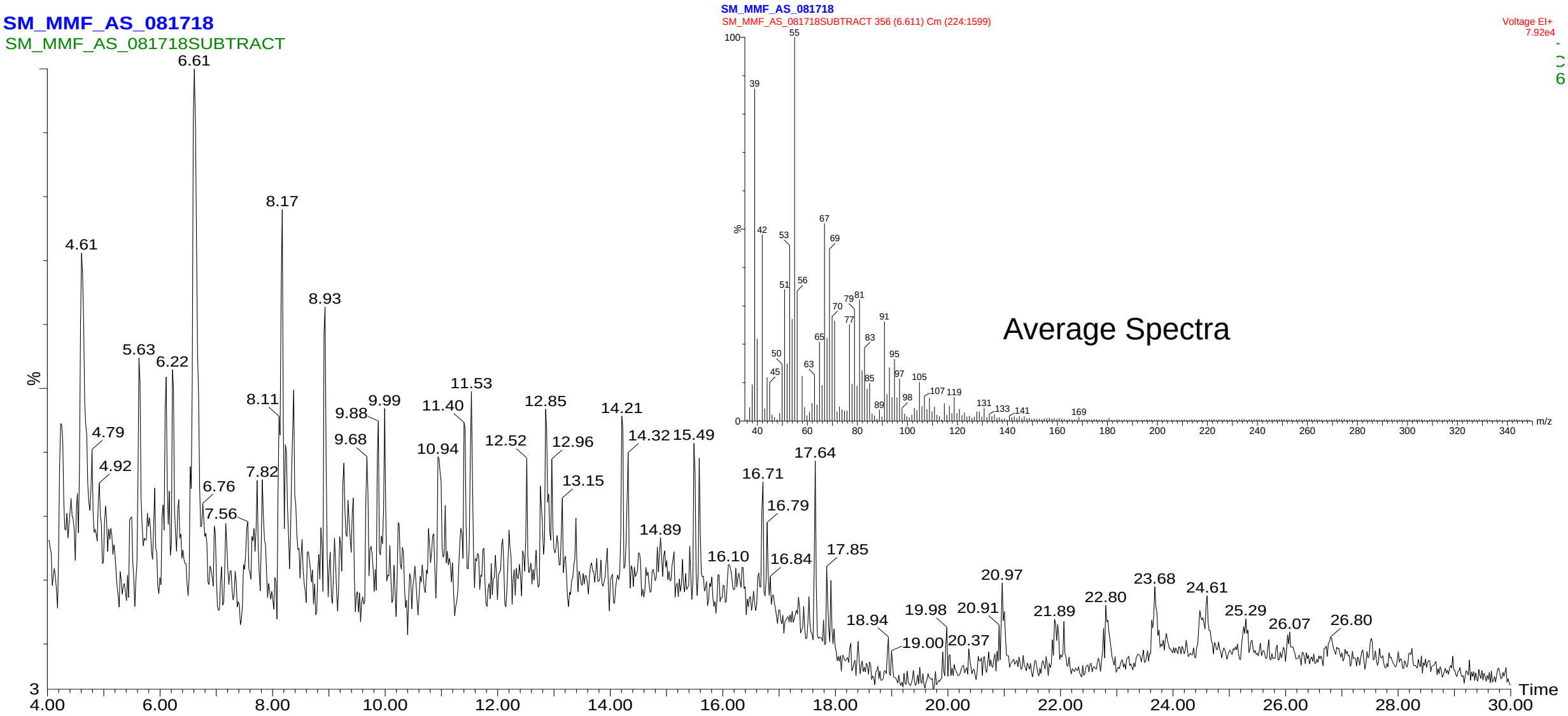
The Mystery Material – Black Flakes



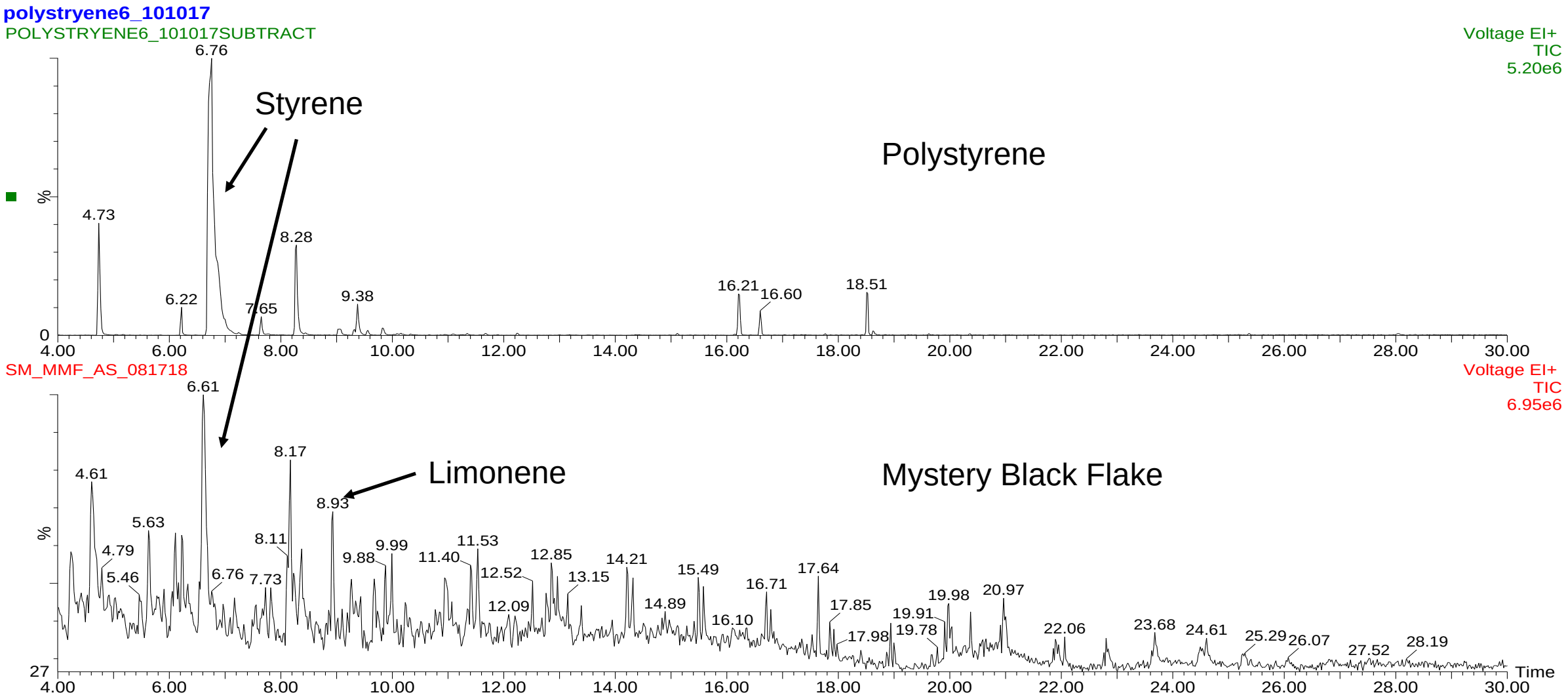


Photos and Materials Courtesy of Sherri Mason and Peter Lenaker

Mystery Black Flake – Pyrogram / Average Spectra



Mystery Black Flake Pyrogram– A Deeper Look

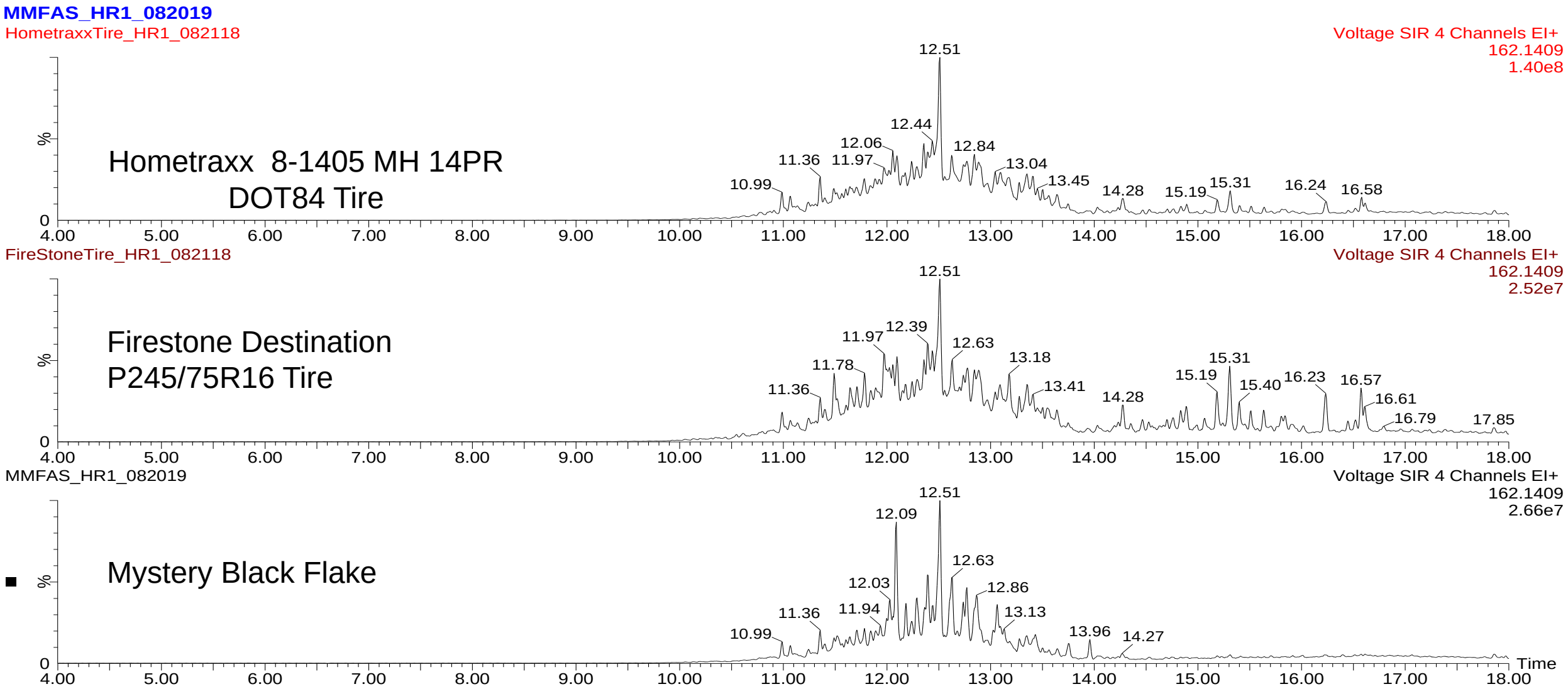


Common Pyrolysis products of Styrene-butadiene[5]

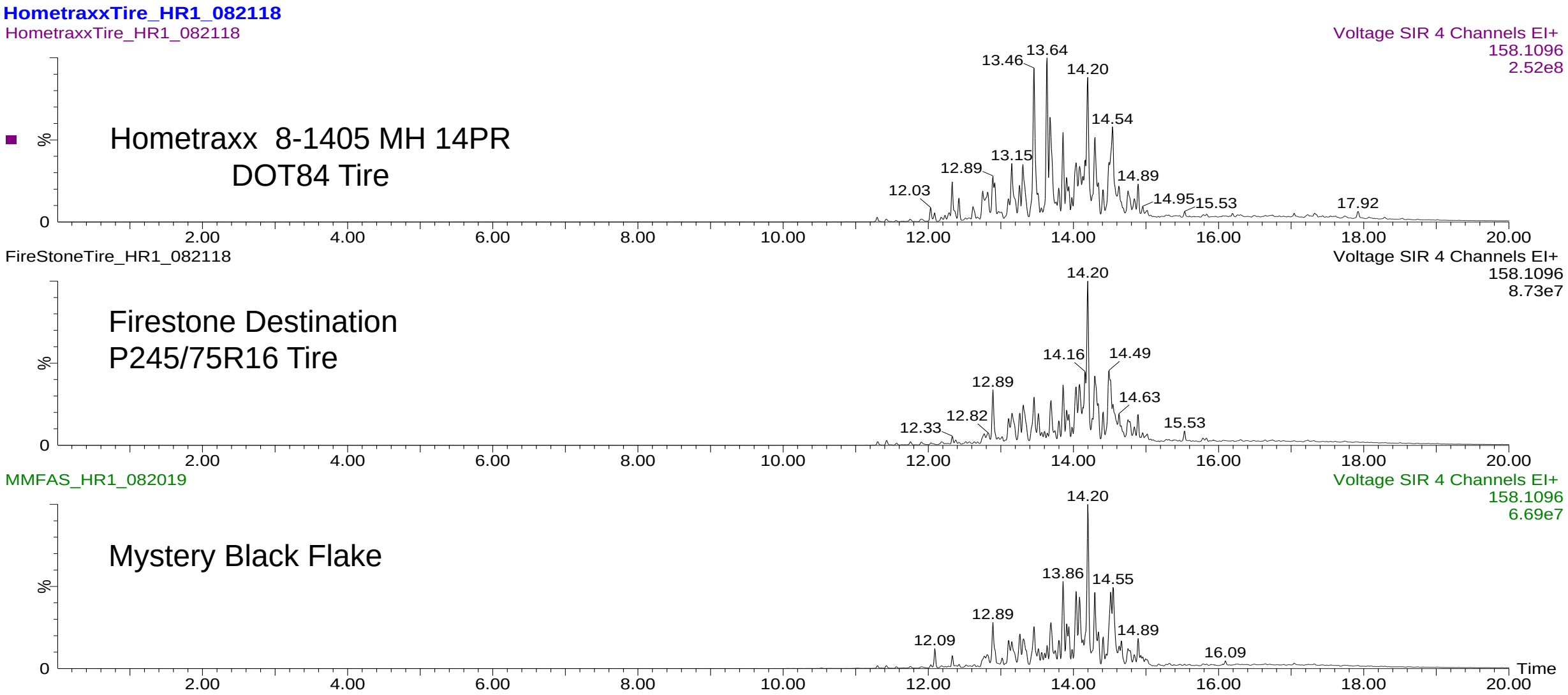
- Xylenes
- Toluene
- Styrene
- Limonene
- Propylbenzene
- Butadiene trimers (BBB) – Accurate Mass 162.1409
- Styrene-butadiene dimers (SB) – Accurate Mass 158.1096
- Styrene-butadiene-butadiene trimers (SBB) - Accurate Mass 204.0939

5- Tsuge, Shin, Hajima Ohtani, and Chuichi Watanabe. *Pyrolysis-GC/MS data book of synthetic polymers: pyrograms, thermograms and MS of pyrolyzates*. Elsevier, 2011.

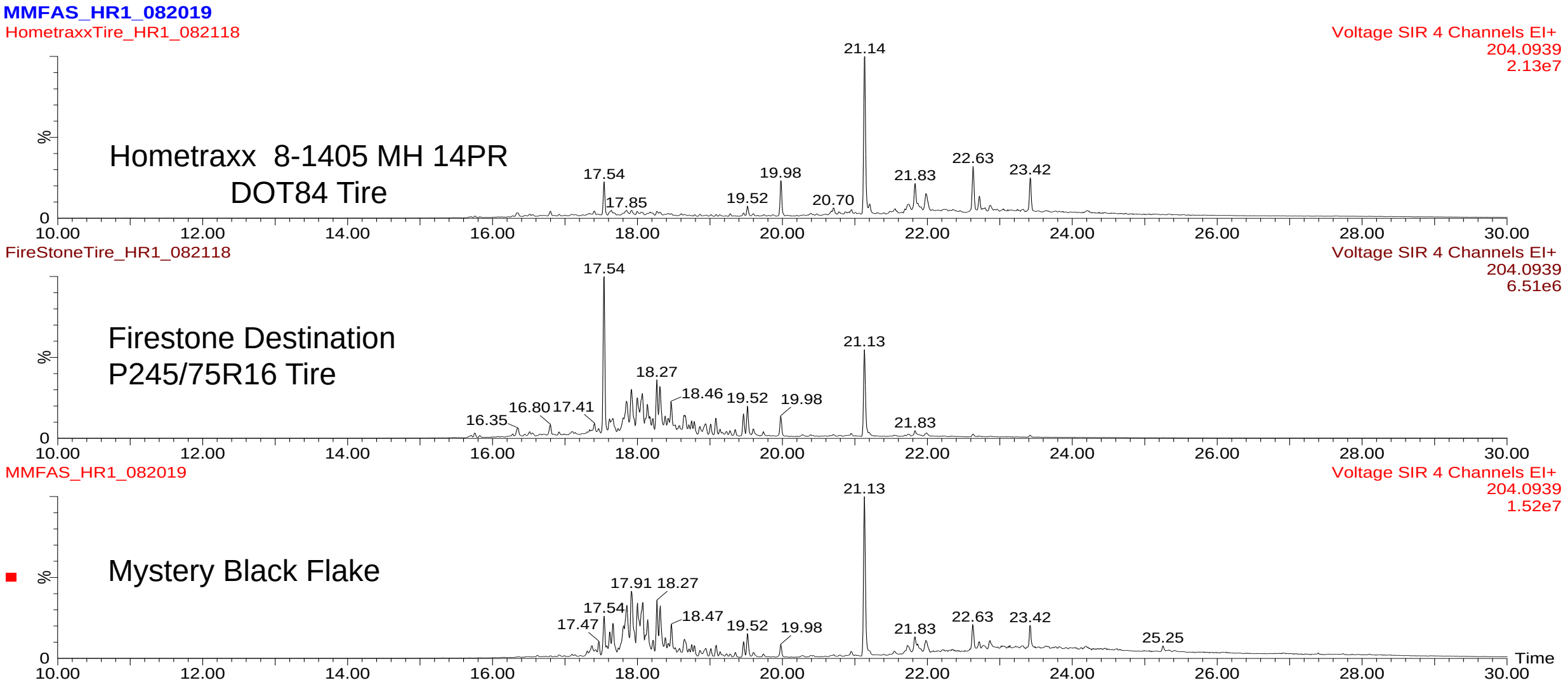
High Resolution Pyrogram - Mass 162.1409 (BBB Trimer)



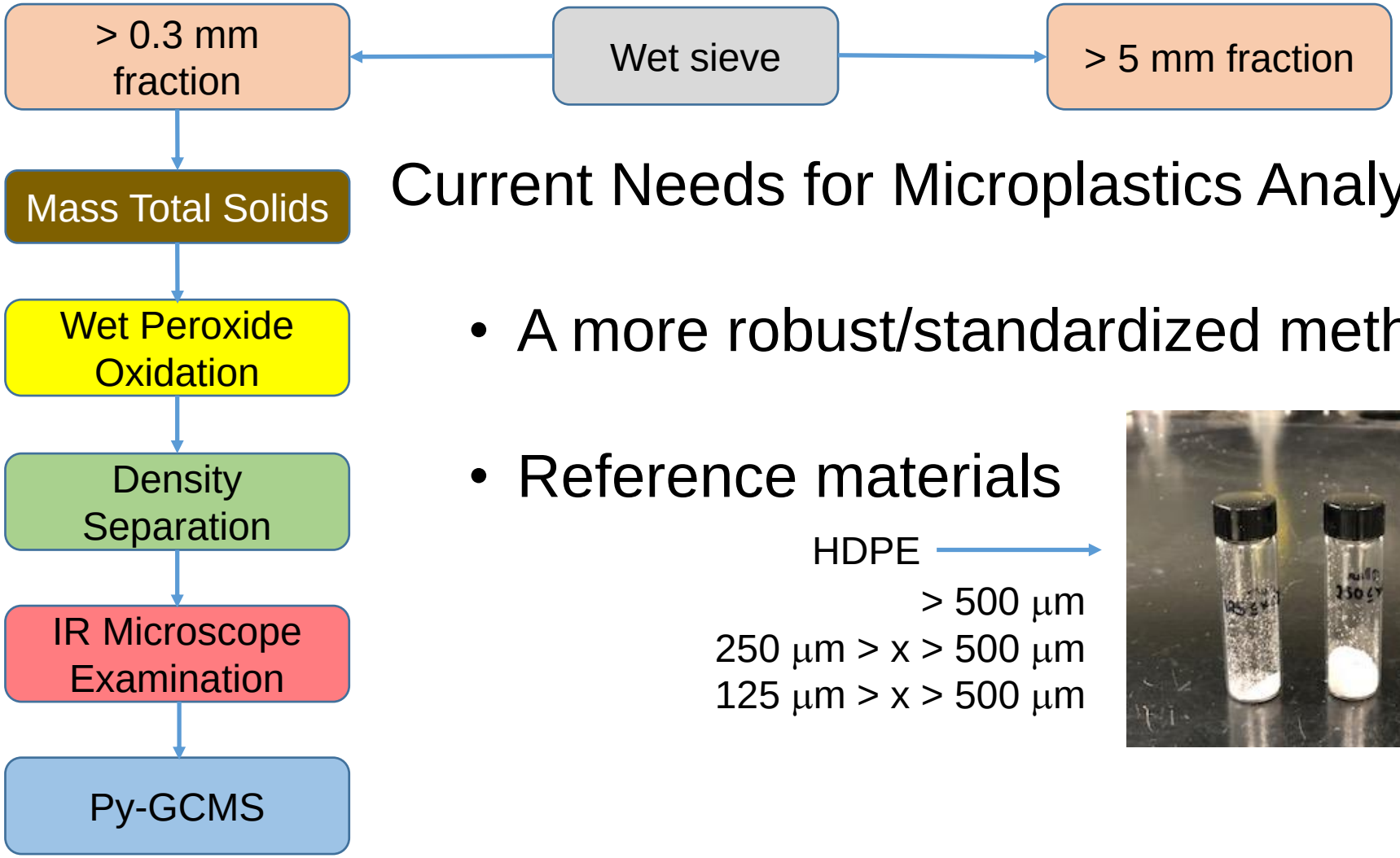
High Resolution Pyrogram - Mass 158.1096 (SB Dimer)



High Resolution Pyrogram - Mass 204.0939 (SBB Hybrids)



Standard Method for Analysis of Microplastics – Waters[6]



Current Needs for Microplastics Analysis

- A more robust/standardized method
- Reference materials

HDPE →

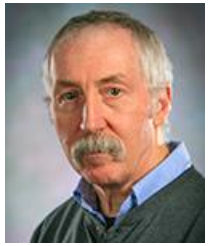
> 500 μm

250 μm > x > 500 μm

125 μm > x > 500 μm

6- Masura, Julie, Joel E. Baker, Gregory Duane Foster, Courtney Arthur, and Carlie Herring. "Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments." (2015).

Acknowledgments - Collaborators



Sam Panno – Illinois Geological Survey

Rae McNeish California State University

Alan Steinmann Annis Water Resources Institute

Stuart Harrad University of Birmingham

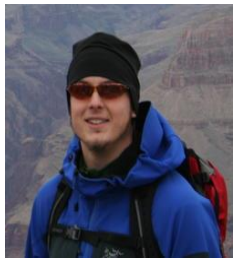
Iseult Lynch University of Birmingham

Tim Leon ISTC

Walt Kelly– Illinois State Water Survey

Kathryn Gunderson ISTC

John Kelly– Loyola University Chicago



Peter Lenaker– United States Geological Survey

Sherri Mason Fredonia New York

Maggie Oudsema Annis Water Resources Institute

Nancy Holm ISTC

Mohamed Abdallah University of Birmingham

Jessica Porter ISTC

Tim Hoellein– Loyola University Chicago

-Rick Rediske Annis Water Resources Institute

Lee Green ISTC

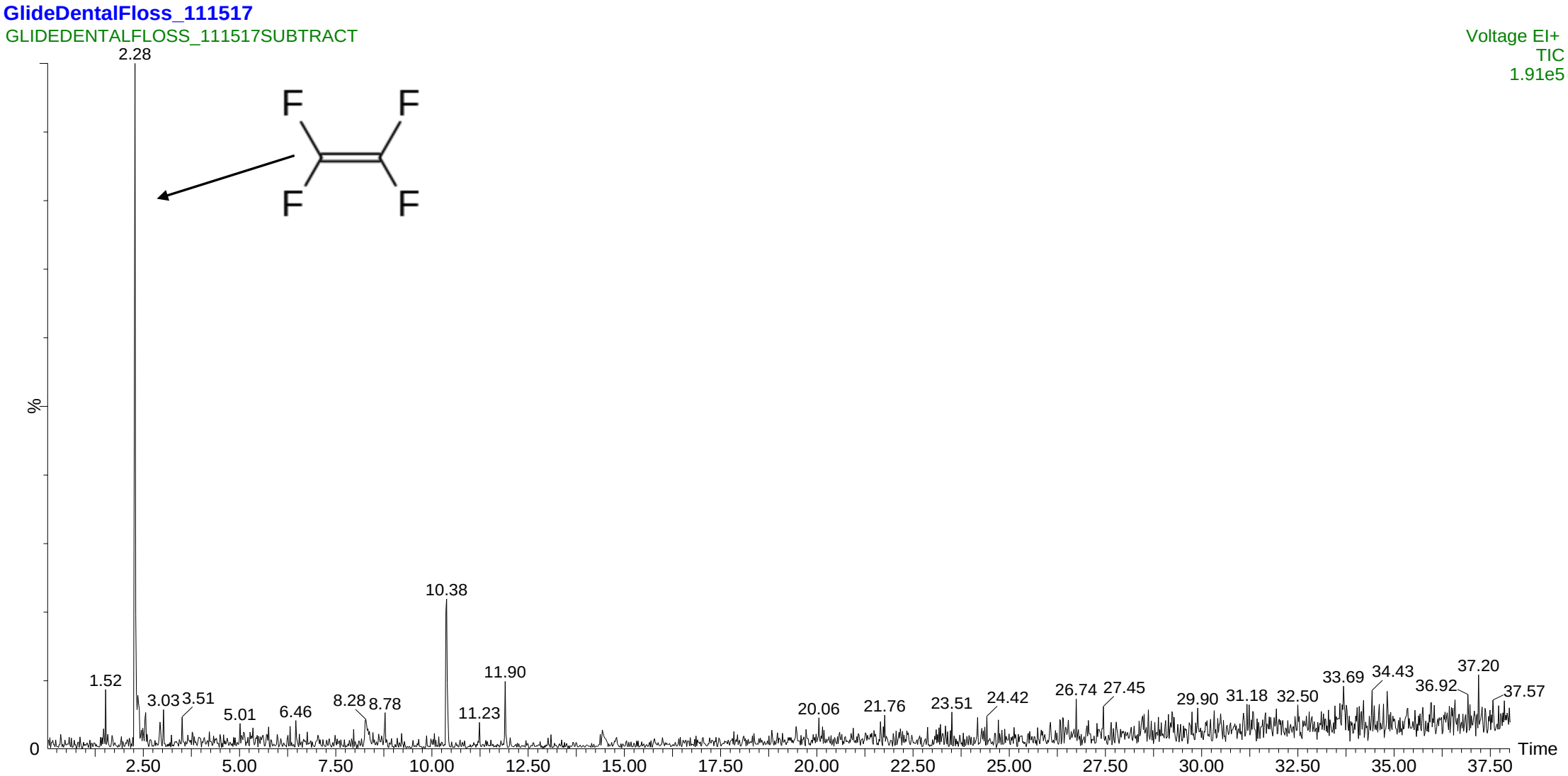
Acknowledgements – Funding Sources

- Allen and Helen Hunting Research and Innovation Fund
- Illinois Hazardous Waste Research Fund (HWR18-253)
- ***B**i**R**imingham**I**llinois Partnership for **D**iscovery, En**G**agement, and **E**ducation*
- Illinois Indiana Sea Grant (NA18OAR4170082)
- University of Illinois Professional Development Fund

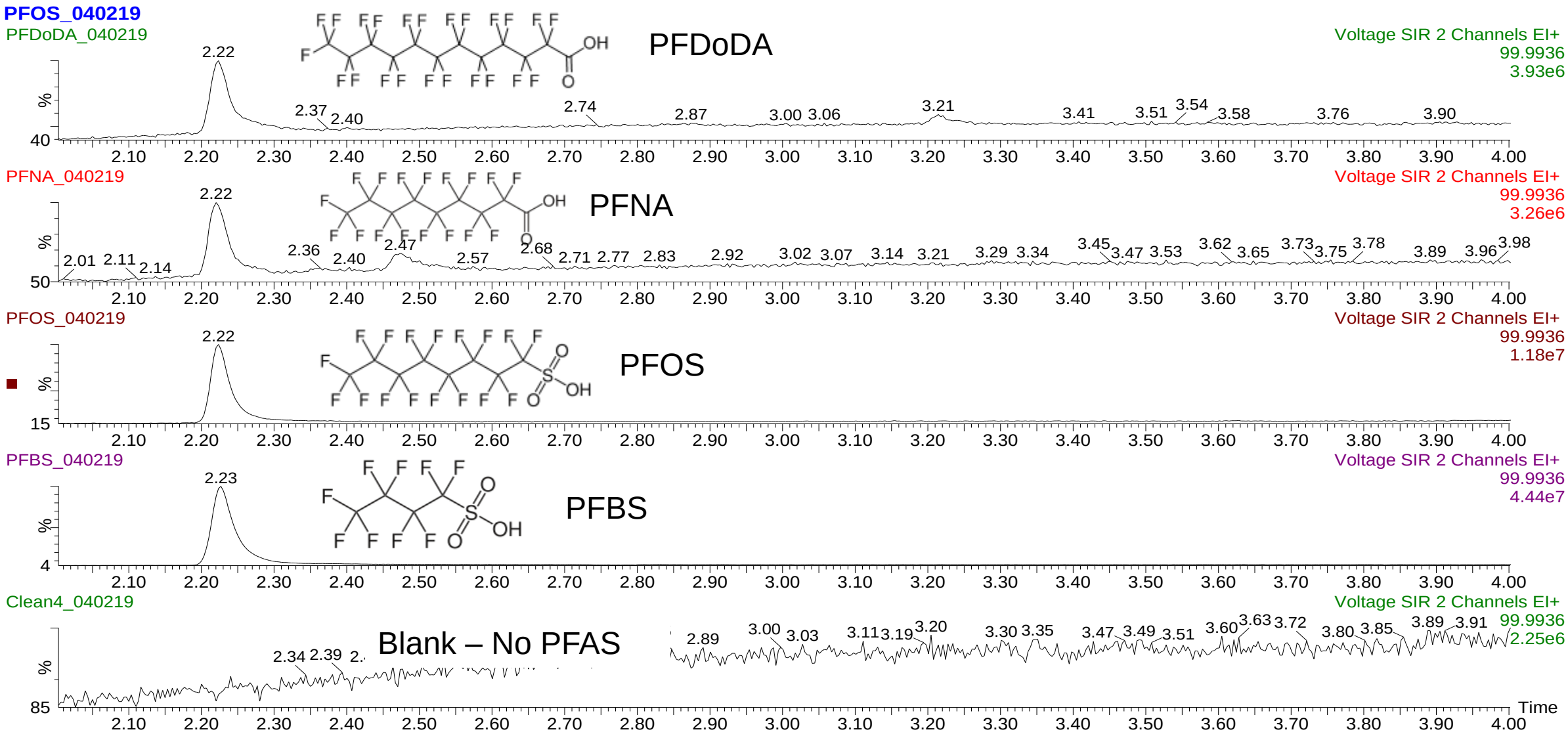
From microplastics to per & polyfluoroalkyl substances (PFAS)

A potential py-GCMS application for screening of PFAS using total organic fluorine

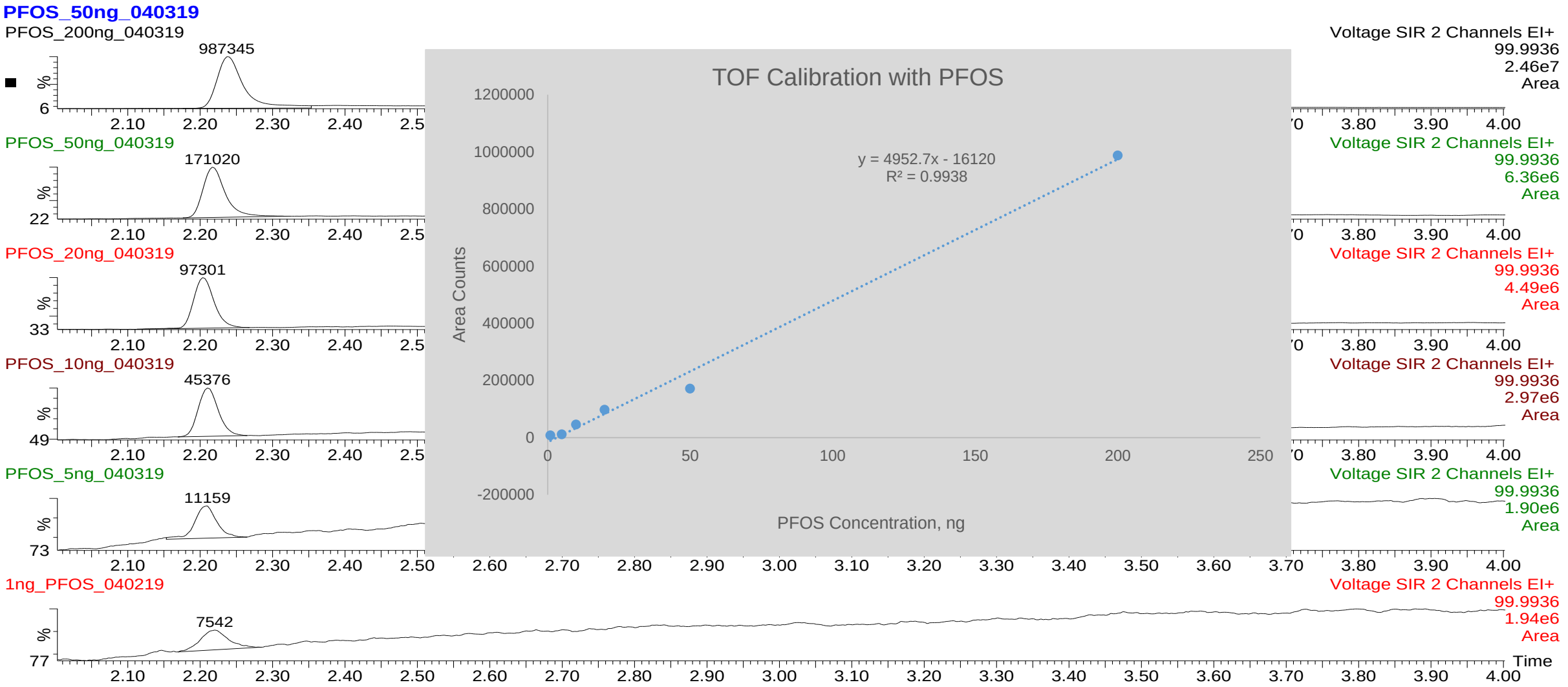
Dental Floss - Pyrogram



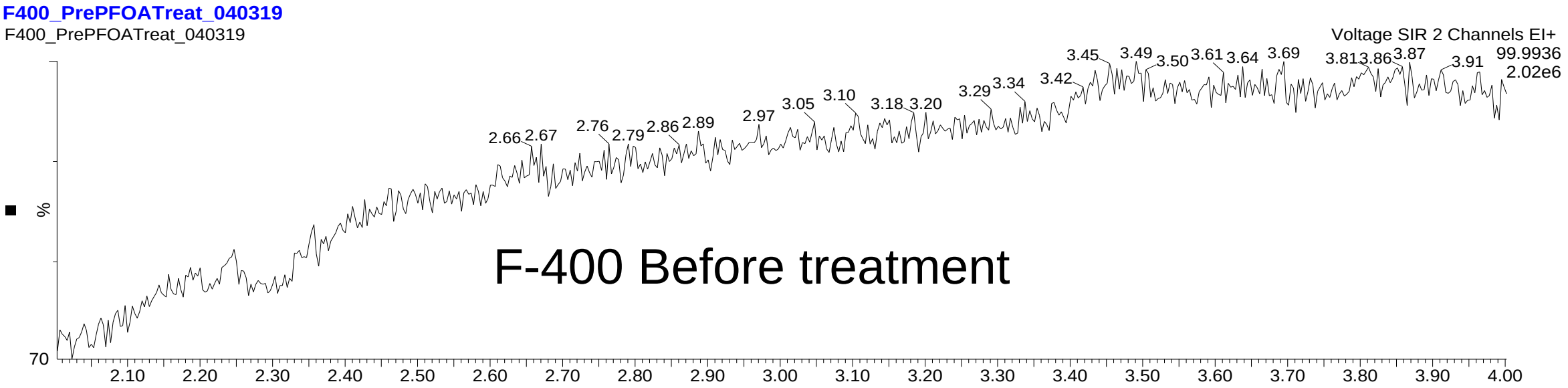
Per & Polyfluoroalkyl Substances (PFAS)

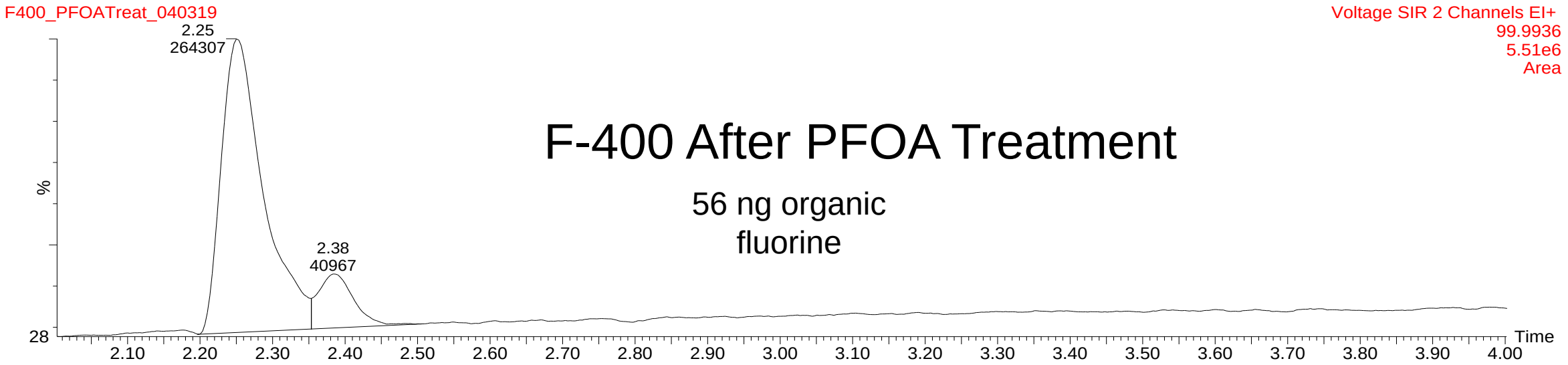


Calibration with PFOS



Total Organic Fluorine – Activated Carbon





Questions?

John W Scott, ISTC Senior Analytical Chemist
zhewang@Illinois.edu
217-333-8407